



A highly active hybrid catalyst modified $(\text{La}_{0.60}\text{Sr}_{0.40})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3-8}$ cathode for proton conducting solid oxide fuel cells



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HIGHLIGHTS

- PNM and PrO_x are impregnated in the LSCF cathode of H-SOFCs.
- Performance of single cells is greatly increased by the impregnation.
- The durability of single cells is also improved by the impregnation.

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ABSTRACT

The sluggish reaction kinetics in the cathode usually leads to considerable cathode polarization resistance, hindering the development of proton conducting solid oxide fuel cells (H-SOFCs) operated at intermediate temperatures (400–650 °C). To address this problem, for the first time, a novel hybrid catalyst consisting of $\text{PrNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and PrO_x is impregnated in the $(\text{La}_{0.60}\text{Sr}_{0.40})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3-8}$ (LSCF) cathode of H-SOFCs, resulting in significant enhancement of the cathode reaction kinetics. Single cells with impregnated LSCF cathode and $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_3$ (BZY) electrolyte yield a maximum power density (MPD) of 0.198 W cm^{-2} at 600 °C, more than doubled of that with blank LSCF cathode (0.083 W cm^{-2}). ECR and EIS studies reveal that the hybrid catalyst can substantially accelerate the oxygen-ion transfer and oxygen dissociation-absorption processes in the cathode, resulting in significantly lower polarization resistance and higher MPD. In addition, the hybrid catalyst possesses good chemical and microstructural stability at 600 °C. Consequently, the single cells with impregnated LSCF cathode show excellent durability. This study shows that the impregnation of this novel hybrid catalyst in the cathode could be a promising approach to improve the performance and stability of H-SOFCs.

1. Introduction

Solid oxide fuel cell (SOFC) has received increasing attention in recent years owing to its high energy-conversion efficiency, broad application range and fuel flexibility [1]. However, the high operation temperature (800 °C–1000 °C) of traditional SOFCs hinders their commercialization and deployment both in portable devices and stationary applications. Therefore, considerable efforts have been devoted to developing intermediate temperature (400 °C–650 °C) SOFCs in the past ten years [2–4]. Proton-conducting SOFC (H-SOFC) has gradually attracted significant research attention for its reduced operation

temperature, relatively low activation energy and high energy efficiency [5–8].

As one of the state-of-the-art electrolytes for H-SOFC, $\text{BaZr}_{1-x}\text{Y}_x\text{O}_3$ (BZY) has garnered particular attention because of its high chemical stability and high bulk proton conductivity [9–14]. However, there are still a number of technical challenges for BZY electrolyte. The sluggish rate of oxygen reduction reaction (ORR) in the cathode, and consequently high cathode polarization resistance, is one of the crucial factors influencing the performance of the H-SOFC cells [15,16]. Among the cathode materials developed for H-SOFCs, $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_3$ (LSCF) cathode, which has been widely studied in oxygen-ion

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conducting SOFC (O-SOFC) [17], has also been applied in H-SOFCs for its high electronic and ionic conductivities [18]. However, the relatively slow kinetics of oxygen dissociation-absorption process limits the performance of LSCF as cathode material for H-SOFCs [19]. To date, the highest maximum power density of H-SOFC with BZY as electrolyte material and LSCF as cathode material is only 0.11 W cm^{-2} at 600°C [20]. Moreover, Sr segregation near surfaces or interfaces of LSCF causes significant degradation of the electrochemical performance and affects its long-term operational life [17].

One effective way to solve the above problems is to modify the surface of LSCF through impregnation with coating of stable and catalytically-active nanoparticles [21]. Ding et al. [22] have reported that the electro-catalysis and stability of LSCF cathode in O-SOFCs can be substantially enhanced by coating the more active Mn-based catalyst. Recently, Chen et al. [23] have reported that the electrochemical performance and stability of LSCF in O-SOFCs could be drastically improved by forming a thin layer of $\text{PrNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (PNM) and PrO_x nanoparticles on the LSCF surface through impregnation of $\text{Pr}_2\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_4$ solution. However, the above studies have been conducted in O-SOFCs but not in H-SOFCs. Unlike the O-SOFCs, protons (H^+) are transported and water is formed at the cathode side of H-SOFCs, making cathode reactions fundamentally different from that of the O-SOFCs, resulting in more sluggish ORR [24,25]. Unfortunately, there have been very limited reports concerning the modification of LSCF cathode by impregnation for H-SOFCs. Although $\text{Y}_{0.25}\text{Bi}_{0.75}\text{O}_{1.5}$, $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) and Ag have been impregnated in the LSCF cathode, these studies have been mainly focused on improving electro-catalytic performance and the effect of the nanoparticle catalyst on the LSCF cathode stability has not been reported yet [19,26,27].

In order not only to enhance the electro-catalysis but also to improve the stability of LSCF cathode in H-SOFCs based on BZY electrolyte, hybrid catalyst consisting of PNM and PrO_x has been impregnated to the LSCF cathode in this study, as shown in Fig. 1. Microstructure characterization shows that the nano-structured modification on the LSCF cathode is obtained. Experimental results demonstrate that the hybrid catalyst on the LSCF surface can significantly enhance the oxygen adsorption and dissociation process of ORR, resulting in substantial reduction in the polarization resistance of the LSCF cathode and enhancement of the H-SOFC cell performance. In addition, the hybrid catalyst can potentially suppress Sr segregation and consequently improve the H-SOFC long-term performance stability.

2. Experimental

2.1. Preparation of powders

The BZY powders were synthesized by a combined EDTA-citric acid method [28]. Metal nitrate precursors $\text{Ba}(\text{NO}_3)_2$ (Alfa Aesar 99%), $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Alfa Aesar 99.9%) and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar 99.9%) were dissolved in deionized water and then titrated by ethylenediaminetetraacetic acid (EDTA). Stoichiometric amounts of metal nitrate solutions were mixed in a beaker and heated at 80°C under stirring. EDTA and citric acid were added to the solution as the chelating agent, with the molar ratio of EDTA/citric acid/total metal cations at 1:1.5:1.

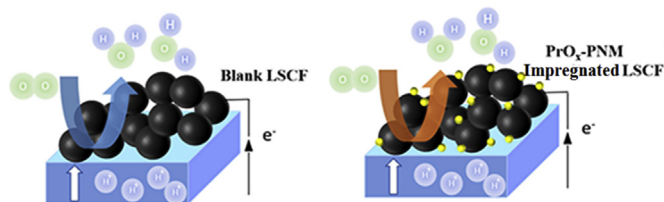


Fig. 1. Schematic illustrations of blank LSCF electrode and PNM- PrO_x impregnated LSCF for H-SOFCs.

Ammonia additions were used to adjust the pH value of the solution to approximately 8. An appropriate amount of ammonium nitrate was then added to trigger combustion. The precursor solution was subsequently heated on a hot plate until self-combustion occurred. The as-prepared ash was fired at 1100°C for 10 h to form the perovskite structure.

The PNM powders were synthesized by a wet chemical method. $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar 99.9%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as the raw materials while citric acid was added as the complexing agent. Other procedures were similar to the above and the fired temperature of the as-prepared ash was controlled at 800°C for 1 h to obtain the final powders.

2.2. Material characterization

To evaluate the chemical compatibility between PNM and BZY, X-ray diffraction (Rigaku MiniFlex II, with $\text{Cu K}\alpha$ radiation and a D/teX silicon strip detector) was used to identify the crystal structures of the sample after each treatment.

2.3. Fabrication of single cells

NiO -BZY electrode supported cells with thin BZY electrolyte layer were fabricated by dry-pressing and drop-coating. NiO powders (JT-Baker, USA), BZY powders and carbon black (average particle size: $1 \mu\text{m}$) were mixed with weight ratio of 5.5:4.5:2. The mixed powders were used to prepare the NiO -BZY electrode substrates (10.3 mm in diameter and 0.3 mm in thickness after sintering at 1450°C) by dry-pressing and then firing at 600°C for 2 h.

The BZY electrolyte slurry was prepared by mixing and ball milling BZY powders, NiO powders (1.0 wt.% of BZY) as sintering aid, ethanol as solvent, TEA as dispersant, Polyvinylbutyral (PVB) as polymer binder, Dibutyl phthalate (DBP) and (polyethylene glycol-600) PEG-600 as plasticizers [29,30]. BZY electrolyte layer was then deposited on the NiO -BZY substrates by drop-coating method, followed by sintering at 1450°C for 5 h.

The $(\text{La}_{0.60}\text{Sr}_{0.40})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3-\delta}$ (LSCF, Fuel Cell material, USA) electrode with an effective area of 0.33 cm^2 was applied onto the surface of the BZY electrolyte layer by using LSCF ink and brush painting method and then sintering at 1000°C for 2 h.

Impregnation procedure: The hybrid catalyst solution used for impregnation was prepared by dissolving $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in molar ratio of 4:1:1 in appropriate amount of deionized water, and then adding glycine as a chelating agent under stirring to form 0.1 M $\text{Pr}_2\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{4+\delta}$ solution. In order to improve the permeability of the solution, ethanol was added and the impregnation process was operated in the vacuum impregnation machine (Struers CitoVac). The hybrid solution was carefully impregnated $6 \mu\text{L}$ on the surface of the LSCF cathode. After that, the assembled cells were fired at 800°C for 1 h, allowing decomposition of nitrate and formation of PNM nanoparticles. The content of infiltration is controlled by dropping accurate amount of the catalyst precursor solution in the cathode. Furthermore, the content of infiltration is determined by measuring the change of weight of the dried sample after infiltration. Finally, 15 wt.% impregnation loading with respect to the weight of LSCF cathode layer is achieved.

2.4. Characterization of the single cells

The prepared single cells were attached to one end of an alumina tube using an electrical conductive paste (DAD-87, Shanghai Research Institute of Synthetic Resins, China). High temperature ceramic adhesives (552-1105, Aremco, USA) were then applied outside the attached cells to avoid gas leaking. $30 \text{ ml min}^{-1} \text{ H}_2$ was fed to the hydrogen electrode side during the test. Hydrogen flow rate was controlled by mass flow controllers (APEX, Schoonover, USA).

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